

## NANOMAGNETISM

## Spin doctors play with single electrons

It is now possible to prepare a semiconductor quantum dot that contains a single magnetic atom, and then add just one extra electron or 'hole' to it, opening up the possibility of a new era in spintronics.

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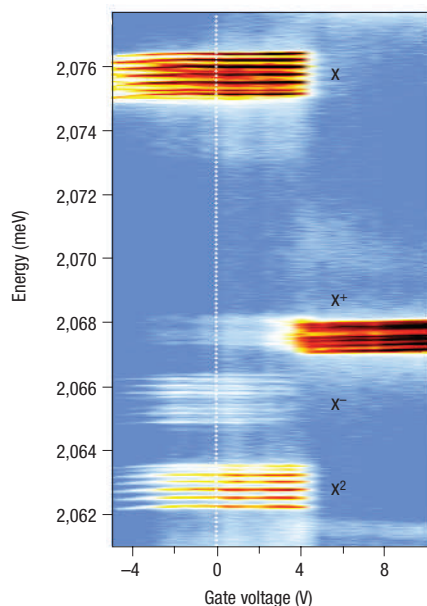
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One of the outstanding scientific advances of the last century was an ingenious experiment that manipulated and detected single electrons. Remarkably, the detection was done optically, and involved measuring the dramatic changes that occur when just one electron is transferred to a microscopic object. The year was 1911, and Robert Millikan would 12 years later win the Nobel Prize for Physics for demonstrating with his oil-drop experiment that electrical charge is quantized in units of  $e = 1.602 \times 10^{-19}$  coulombs. And although this experiment was unquestionably a technical *tour de force*, Millikan's real breakthrough was to focus on measuring individual drops of oil rather than ensembles (or 'swarms' as Millikan dismissively called them). This was important because measurements on ensembles could only have revealed the average properties of the drops, but they would not have allowed Millikan to show so convincingly that electric charge was quantized.

A century later the manipulation and detection of single electrons is still a challenging area of research. One especially fascinating line of work aims to use single electrons as precision tools for manipulating other electrons. Writing in *Physical Review Letters*, Yoan Léger, Lucien Besombes and co-workers<sup>1</sup> at the CNRS Laboratoire de Spectrométrie Physique in Grenoble, France, the Joseph Fourier University, also in Grenoble, and the University of Alicante in Spain, report a significant step toward this goal, by first inducing a single electron to interact with the magnetic moment or 'spin' of an isolated manganese atom, and then detecting the dramatic effects of these interactions optically — a modern analogue to Millikan's pioneering experiment.

However, the oil drops have given way to cadmium telluride quantum dots, which are



**Figure 1** The photoluminescence signal from a quantum dot containing a single Mn atom, plotted as photon energy (y axis) versus bias voltage<sup>1</sup>. A laser is used to create an exciton in the quantum dot, and the interactions between this exciton, the Mn atom and extra electrons or holes that are added to the dot, result in a series of emission lines in the photoluminescence spectrum. The figure shows the spectra for a neutral exciton (X) and three charged excitons (X<sup>+</sup>, X<sup>-</sup> and X<sup>2-</sup>). Copyright (2006) APS.

grown by molecular-beam epitaxy within a zinc telluride matrix<sup>2</sup>. During the growth process, individual Mn atoms were allowed to diffuse into the quantum dots and replace single cadmium atoms — a technique that was developed about a decade ago<sup>3</sup>. Single electrons were transferred on and off the quantum dots using two methods. In the electrical gating approach<sup>4</sup>, a voltage applied to the ZnTe substrate causes an electron to move from the dot to the substrate, leaving a positively charged 'hole' on the quantum dot. In resonant optical excitation<sup>5</sup>, on the other hand, a photon from a laser transfers just enough energy to an electron in the

ZnTe to excite it into the next energetically available state, which is in the CdTe dot. Finally, the interaction between the spin of the Mn atom and the spin of the extra electron or hole was probed optically, not with the microscope of Millikan's experiment, but by measuring the spectrum of the photoluminescence that is emitted when an electron and hole recombine to emit light.

How can single electrons be used to manipulate spins? In bulk crystals of semiconductors that have been lightly doped with Mn, the addition of extra holes can give rise to ferromagnetic interactions within the 'swarm' of Mn spins, providing a spectacular example of collective manipulation. This phenomenon gave birth in the mid-1990s to the field of semiconductor spintronics<sup>6</sup>, which seeks to marry the advantages of semiconductors and magnetism within the same material.

Macroscopic ferromagnetism is not possible in a single quantum dot, but equally striking phenomena can take place when charge carriers (electrons and holes) are confined to nanoscale dimensions<sup>7</sup>. For example, if the wavefunction of a charge carrier is confined to a dimension that is smaller than its normal Bohr radius, its interaction with the spin of a Mn atom greatly increases. Theorists have explored what happens when the size of a quantum dot containing two Mn atoms and a hole is varied<sup>8,9</sup> but no one has managed to do this experiment in the lab, partly because it is very difficult to detect tiny changes in the magnetic interaction between two atoms.

Léger's method for detecting changes echoes Millikan's: to measure the influence of an added electron or hole on just one Mn spin. For this task the technique of photoluminescence spectroscopy literally shines. The spectrum of radiation emitted when an electron and hole recombines directly reflects the energy distribution of the available quantum states before recombination (that is, in the initial excited state) and also afterwards (in the final state). These distributions contain most of the information we need to know about the

conditions experienced by charge carriers inside the quantum dot.

Photoluminescence spectroscopy has become a standard tool for characterizing neutral quantum dots that do not contain magnetic dopants: in these experiments a laser creates an excited electron–hole pair, also known as a neutral exciton, which almost immediately recombines back to the ground state, emitting a photon in the process. The resulting photoluminescence spectrum is particularly simple, because there are relatively few initial and final states and, moreover, some transitions are forbidden by ‘selection rules’ that enforce conservation of angular momentum.

Things get more complicated when a Mn dopant is included in the quantum dot, because the exciton can now interact with the five outermost electrons in the 3*d* shell of the Mn atom. Each of these electrons carries a spin of 1/2 in quantum units, and they invariably align themselves so that the total spin, *S*, has a value of 5/2. A measurement of *S* along any direction, for example the *z* axis, must yield a quantized result having one of six possible values: *S<sub>z</sub>* = +5/2, +3/2, +1/2, −1/2, −3/2 and −5/2. This leads to a splitting of the once-simple photoluminescence spectrum into six equally spaced components<sup>10</sup>.

Léger’s experiment<sup>1</sup> takes the logical next step, by adding an electron or hole and observing how the photoluminescence

spectrum changes. By now the system may seem hopelessly complicated: the quantum dot contains one Mn atom (with five 3*d* electrons), one electron–hole pair (the exciton created by the laser), and the extra electron or hole (from gating or resonant optical excitation). But simplification is possible. Consider a negative quantum dot containing one extra electron and one Mn atom. In much the same way that the five 3*d* electrons of the Mn atom align to form a single *S* = 5/2 spin, the extra electron and the electron from the exciton lock together with their spins pointing in opposite directions to form a single *S* = 0 object, which has no magnetic interactions with the Mn atom. Hence for the initial state of the system one need only consider the interaction of the hole with the Mn spin. After recombination, there is just one electron interacting with the Mn spin. The picture is equally simple for a positive quantum dot containing one extra hole and one Mn atom.

The bottom line of the analysis is straightforward: the six-line spectrum should be split by the presence of an additional electron or hole into 12 distinct lines, less one that is forbidden by selection rules. These 11 lines can be seen clearly in the beautiful spectra recorded by Léger and co-workers (Fig. 1). Moreover, by measuring the spacing between lines, they show that the electron–Mn and hole–Mn interactions are affected by

the confinement of the charge carriers inside the quantum dot just as expected theoretically. Such manipulation and detection of single electrons on an individual atom within a quantum dot are important steps towards the writing and reading of digital information at extremely small scales.

No one knows for certain what nanotechnologies will exist another hundred years from now. Feynman’s famous dictum ‘there’s plenty of room at the bottom’ will someday drive us further down a winding road that already includes oil drops and quantum dots. And if history is any guide, using single electrons to manipulate and detect other electrons will doubtless play a central role along the way. We can only marvel at where we’re heading.

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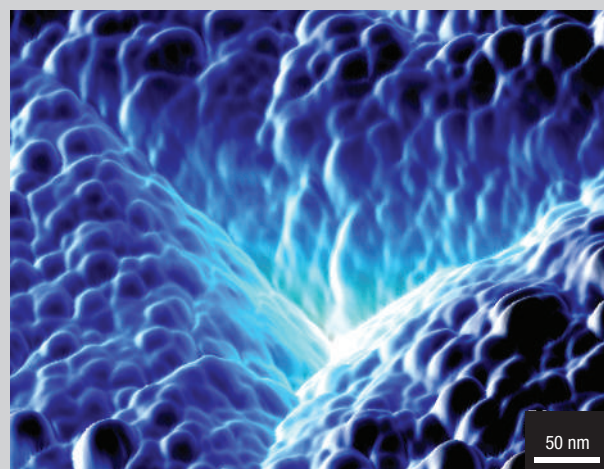
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## Biomaterials: Close to the bone

Our bones have to be able to withstand many types of impact. Daily activities such as walking, for instance, require a certain amount of elasticity, but the bones in our heels and back are often subject to sudden jolts that compact bone fibrils. Understanding more about the mechanisms that prevent our bones from fracturing under such compressive loads will help in the treatment of problems that result from old age, disease and injury. This is why Christine Ortiz and colleagues at the Massachusetts Institute of Technology are exploring the nanostructural origins of bone strength (*Nano Lett.* doi:10.1021/nl061877k; 2006).

The carbon-based mineralized platelets that coat the collagen fibrils in our bones are known to provide increased strength

under tension (pulling). But, how do these minerals affect the elastic response of bone when the fibrils are squeezed together? Ortiz and co-workers wanted to check if the frictional interactions between these minerals helped bones to resist cracks and failure under compression. They combined nanoindentation — which involves pushing a sharp tip into a material — and atomic force microscopy to study how bone responds to compressive forces on sub-10-nm length scales (see image). Their results show that normal bone has a greater resistance to compressive stress than demineralised bone, and that cohesion and friction between the mineralized platelets help them to compress easily, rather than slip. Ortiz’s findings are consistent with what



AFM image of a nanoindentation in the outer layer of an adult bovine bone.

is observed in nature: tendons, which respond to tension, contain no minerals, whereas whale bones, which must sustain large compression forces, are almost entirely made of minerals.

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